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Adsorption Characteristics of Carbon Sorbents from Naturally Oxidized Barzas Coal

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Abstract

The paper studied adsorption characteristics of carbon sorbents produced from naturally oxidized coal of Barzas deposit. Synthesis of sorbents was carried out by the chemical activation method using potassium or sodium hydroxide and carbonization at 800 °C. The effect of alkaline nature and the amount of the introduced alkali at the impregnation stage on characteristics of the resulting sorbents was studied. Adsorption characteristics were explored on an example of benzene, phenol, and iodine. Benzene adsorption under the studied conditions linearly depends on the total pore volume in the sorbent. It was demonstrated that sorbents produced from the naturally oxidized Barzas coal activated by potassium hydroxide had the developed porous structure and high adsorption characteristics. To produce sorbents with high characteristics from the naturally oxidized Barzas coal with potassium hydroxide activation it was sufficient to use a coal/KOH mass ratio of 1 : 0.5.

Keywords: carbon sorbents, oxidized coal, carbonization, porous structure, adsorption

INTRODUCTION

Environmental problems concerning pollution of water resources currently remain their relevance. The quality of some natural water sources is often unacceptable to use them for food purposes and technical needs. Hazardous organic substances, heavy metals, and radionuclides may be present in water bodies, often in quantities that significantly exceed MPC, therefore, this water is not high-quality and in need of treatment. The use of carbon sorbents (as a part of treatment process or as its major step) in this area is relevant. Herewith, it is worth noting that the production level of domestic brands of carbon sorbents remains low.

There are various schemes of producing carbon sorbents that include preparation and modification of the initial coal and carbonization followed by carbonate activation with a gas or a chemical reagent. Modification stages may strongly vary or be completely absent. Carbonization, *i.e.* heating coal to high temperatures, initiating partial decomposition processes therein with the release of gaseous products that, in turn, and form porous structure is an invariable process for producing carbon sorbents.

Naturally oxidized coal may be utilized as initial raw materials for producing carbon sorbents. The major difference of the former is a relatively low occurrence depth, therefore,

the organic mass of coal acquires a new set of different oxygen groups resulting from weathering under reservoir conditions [1]. Naturally oxidized coal exhibits high activity towards alkalis due to the presence of functional groups of this type. Alkaline chemical activation of naturally oxidized coal followed by carbonization of coal-alkali mixture leads to the generation of developed porous structure of the resulting sorbents, as demonstrated in papers [2–4]. The present work decided to use the above method to produce carbon sorbents from Barzas coal.

Strength properties, textural (BET surface, pore volume and pore diameter) and sorption characteristics (adsorption activity, extraction ratio, and adsorbent capacity for the substance) are considered to be the major features of sorbents. Adsorption activity (measured in the percentage by the technique approved by GOST or as the mass of the absorbed pollutant towards the sorbent mass) is one of the important characteristics of the used sorbents during treatment from pollutants. Iodine, phenol, and benzene are often used as reference substances.

The goal of the carried out work was to study adsorption characteristics and regularities of sorption of benzene, phenol, and iodine by carbon sorbents produced from naturally oxidized coal of Barzas deposit *via* the method of carbonization of various composition coal.

EXPERIMENTAL

Coal from the Barzas deposit sampled in the area of the Barzas village with a depth up to 3 m from the zone of weathering was taken to produce sorbents. Afterwards, a coal sample was crushed to the particle size of less than 3 mm and rinsed with water to remove clay inclusions. Coal with the particle size less than 0.2 mm was used for analytical studies.

Studies of characteristics of initial coal were carried out in accordance with ISO 602–74 and ISO 562–74 (technical analysis) and ISO 625–75 (elemental composition) standards. Ash for chemical analysis was produced by slow ashing of the coal sample in a muffle furnace at 815 °C. Qualitative and quantitative composition

of ash-forming components was determined by atomic emission spectroscopy using iCAP 6500 Duo LA instrument (Thermo Scientific, USA). The composition of the organic mass of coal was determined by elemental analysis techniques using ThermoFlash-2000 CHNOS analyser. Oxygen content in the active phase was defined as its total amount in the form of phenol, carbonyl, and carboxyl groups, and in the inactive form – by the difference in total oxygen and oxygen in the active form. The number of carbonyl groups was set *via* the reaction with hydroxylamine hydrochloric, carboxyl groups – using the acetate method, the sum of carboxyl and hydroxyl groups – by ion exchange with NaOH.

Obtaining sorbents was carried out by the carbonization method (thermolysis) in the presence of alkali by the technique described in [2, 3]. Coal with a particle size smaller than 0.5 mm was used. A sample weight of crushed coal was impregnated for 24 h with a 50 % alkaline solution. Its amount was introduced in such a way for coal/alkali mass ratio to be predetermined i.e. 1 : 0.5; 1 : 1; 1 : 2. Afterwards, the mixture was dried, placed in closed ceramic crucibles, and directed into a muffle furnace for carbonization. Thermolysis consisted of two stages, such as heating to 800 °C with a rate of 7–9 °C/min and ageing at 800 °C for 60 min. The crucibles were then taken of and placed in a desiccator for cooling. The sintered carbonized residues were crushed to a particle size of less than 1 mm, then subsequently washed out from the alkali with distilled water, a 0.1 M HCl solution and then with distilled water again, whereupon the samples were dried to constant mass in an oven at 105 °C.

The study of sorbent porous structure, including the specific surface (S_{BET}), the total pore volume (V_t), and the volume of meso- (V_{me}) and micropores (V_{mi}), was carried out using ASAP-2020 analyzer by low-temperature nitrogen adsorption technique. Measurements of adsorption-desorption isotherms were carried out in the region of equilibrium relative pressures of nitrogen vapours from 10^{-3} to 0.995 p/p_0 . Prior to carrying out measurements, sorbent samples were vacuumed at 200 °C for 720 min and a residual pressure of $5 \cdot 10^{-3}$ mm Hg.

The measurement of the activity of sorbents was carried out according to statistic sorption of

benzene vapours (A_b), phenol (A_{ph}) and iodine sorption (A_i) from an aqueous solution. The static maximum sorption of benzene vapours was measured by the mass gain of the sorbent, placed into the atmosphere of benzene vapours for 24 h. The measurement of phenol sorption was carried out according to calibration dependence using a spectrophotometer, measuring the concentration of phenol left after sorption. The study of the sorption dependence for iodine was carried out by titration of iodine left after sorption with sodium thiosulphate (GOST 6217-74).

RESULTS AND DISCUSSION

Characteristics of a sample of naturally oxidized coal from Barzas deposit used during synthesis of sorbents are presented in Tables 1. Functional composition, mgE/g per daf: >C=O 1.11, -COOH 0.21, OH 1.28; oxygen, % per daf: in active groups 3.6, in inert groups 10.8. Chemical composition of ash of naturally oxidized coal, mass %: SiO₂ 15.0, Al₂O₃ 15.4, Fe₂O₃ 12.8, CaO 35.0, MgO 5.5, TiO₂ 1.6, Na₂O 1.2, K₂O 0.2, P₂O₅ 1.3, SO₃ 12.0. The initial oxidized coal is characterized by relatively high ash content (11.8 %), high content of heteroatoms (14.4 % per daf) and the presence of oxygen-containing functional groups including active (3.6 % per daf), as can be seen from the results of the technical analysis. Analysis of the mineral part detected high contents of calcium, and also aluminium, silicon, iron, and sulphur.

In this work, six different samples of carbon sorbents from naturally oxidized coal of Barzas deposit were synthesized. Nitrogen adsorption-desorption isotherms of the synthesized sorbents were obtained using ASAP 2020 analyzer. Isotherms for all sorbents obtained in the work are similar and typical for microporous samples.

Figure 1 presents nitrogen adsorption-desorption isotherms for sorbents produced

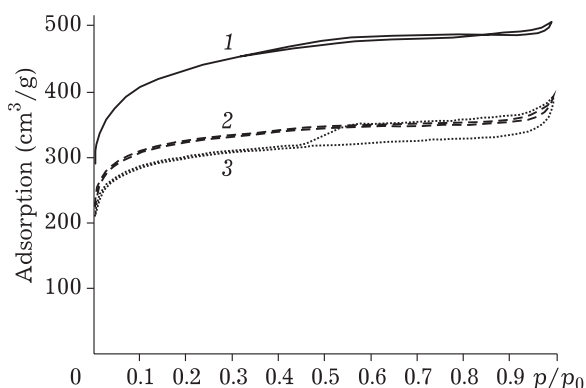


Fig. 1. Nitrogen adsorption-desorption isotherms by samples of carbon sorbents 1-3 (1-3) produced from naturally oxidized coal of Barzas deposit at 77 K (sample numbers correspond to Table 2).

from Barzas coal impregnated with KOH with the coal/alkali mass ratio of 1 : 2 (1), 1 : 1 (2) and 1 : 0.5 (3). The presented isotherms have the initial area of fast filling of micropores, then, their saturation happens, as expressed in the output of the isotherm onto a plateau at high p/p_0 values. The area that's parallel to the axis of relative pressures is found at values close to the value of the maximum adsorption. In isotherms of samples 1 and 2, there is a plot with a narrow hysteresis loop, indicating low contribution of mesopores into nitrogen adsorption. In isotherm of sample 3, there is a pronounced hysteresis relatively to isotherms of samples 1 and 2.

Carbon sorbents have narrow pore distribution (Fig. 2); pores with the sizes less than 20 nm significantly prevail. For sample 3, the contribution of pores with a diameter greater than 20 nm is much higher than for samples 1 and 2, resulting in the hysteresis loop for this sample shown in Fig. 1.

Alkaline nature during obtaining coal samples has a significant effect on the activation process of the initial coal and therefore, on properties of the resulting sorbents [5].

TABLE 1

Characteristics of a sample of naturally oxidised coal of Barzas deposit

Technical analysis, %			Elemental composition, % per daf			Atomic ratio	
W^a	A^d	V^{daf}	C	H	(O + N + S)	H/C	O/C
1.5	11.8	70.2	77.8	7.8	14.4	1.20	0.14

Note. W^a – moisture of analysis sample, A^d – ash content, V^{daf} – yield of volatile matter.

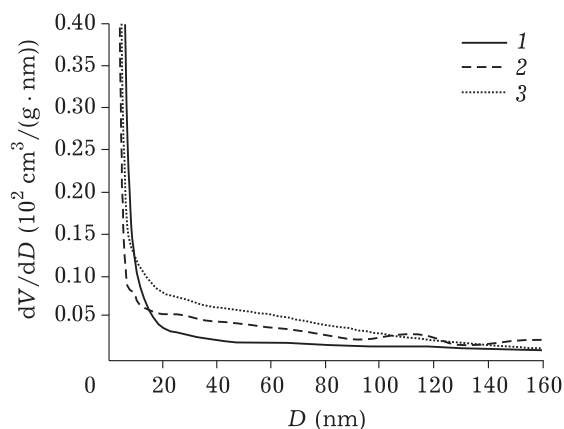


Fig. 2. Differential distribution of pore size in samples of carbon sorbents 1–3 (1–3) produced from naturally oxidized coal of Barzas deposit (sample numbers corresponds to Table 2).

Table 2 gives characteristics of the porous structure of sorbents (S_{BET} – specific surface, V_t – total pore volume, V_{mi} – micropore volume, V_{me} – mesopore volume), and also their sorption activity for benzene (A_b), phenol (A_{ph}), and iodine (A_i). Analysis of the findings demonstrates that carbon sorbents with more developed specific surface and larger pore volume are obtained from Barzas coal *via* thermolysis in the presence of KOH than in the presence of NaOH. Iodine is equally sorbed by the presented samples from an aqueous solution, however, there is much more phenol and benzene for sorbents obtained during chemical activation of KOH.

It can be seen that an increase in the amount of the introduced KOH during chemical

activation of Barzas coal leads to a rise in all textural and adsorption characteristics of the resulting sorbents. However, with increasing the amount of KOH used in synthesis from 0.5 to 2 in relation to the mass of coal (4 times), specific surface of sorbents increases only by 40 %, the total pore volume – by 37 %, herewith, an increase in micropore volume is 25 %, adsorption for benzene increases by 30 %, for phenol – 15 %; an increase in iodine sorption is less than by 10 %. Thereby, a significant increase in the amount of KOH used leads to not so significant improvement of characteristics of sorbents.

Mesopore volume does not correlate with the amount of the introduced alkali. Apparently, coal-alkali ratio during developing mesoporous structure in Barzas coal sorbents is not a prevailing factor.

To understand the total picture of the progression of the sorption process in carbon sorbents the relationship of characteristics of the synthesized carbon sorbent from the naturally oxidized Barzas coal and adsorption activity for benzene, phenol, and iodine was explored. Samples 1–4 were synthesized from coal with a particle size of less than 0.5 mm; for samples 5 and 6, the size of coal particles was 0.2–0.5 and 0.5–1.0 mm, respectively [6].

From the data of Table 2, it can be seen that adsorption activities for phenol and for benzene, BET surface, and the total pore volume and micropore volume are minimum for sorbents activated with NaOH. However, sample 4 has relatively high activity for iodine even with these low characteristics. Activity for iodine is

TABLE 2

Characteristics of carbon sorbents prepared from naturally oxidised Barzas coal activated by alkali

Sample	Alkali	R_o	d , mm	S_{BET} , m ² /g	V_t , cm ³ /g	V_{mi} , cm ³ /g	V_{me} , cm ³ /g	A_b , mg/g	A_{ph} , mg/g	A_i , mg/g
1	KOH	1:2	<0.5	1590	0.77	0.40	0.17	760	172	423
2	KOH	1:1	<0.5	1210	0.58	0.34	0.12	630	149	397
3	KOH	1:0.5	<0.5	1120	0.56	0.32	0.20	590	150	395
4	NaOH	1:2	<0.5	330	0.18	0.07	0.06	290	43	392
5	KOH	1:2	0.2–0.5	1690	0.82	0.42	0.17	800	142	472
6	KOH	1:2	0.5–1	1590	0.75	0.44	0.13	710	133	460

Note. R_o – coal-alkali ratio, d – coal particle size, S_{BET} – specific surface, V_t – total pore volume, V_{mi} – micropore volume, V_{me} – mesopores volume, A_b – adsorption activity for benzene, A_{ph} – adsorption activity for phenol, A_i – adsorption activity for iodine.

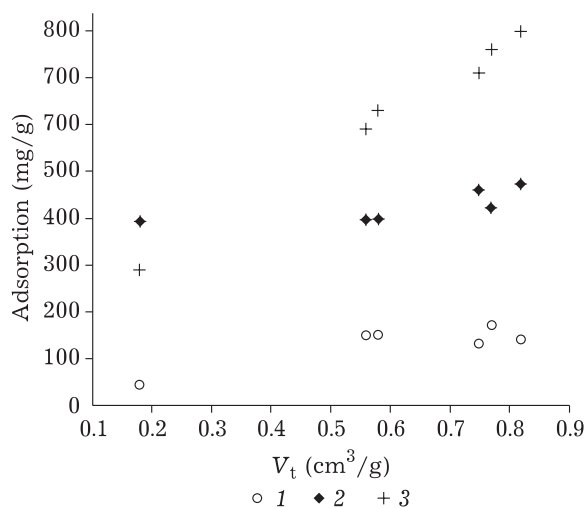


Fig. 3. Experimental values of adsorption of phenol (1), iodine (2), and benzene (3) versus total specific pore volume in carbon sorbents (V_t).

almost identical for all six samples of carbon sorbents and lies within 39–48 %.

The results of the graphical processing of experimental data are presented in Fig. 3, where the dependence of the amount of the adsorbed substance on the total pore volume of carbon sorbents (V_t) is displayed. The scale for the dependencies was selected in such a way to present those for all three substances in one figure.

Figure 3 demonstrates that the total pore volume in the 0.1–0.9 cm³/g range affects the sorption of different substances in a different manner. The values of iodine adsorption (2) do not significantly depend on the total pore volume in samples, weakly increasing in the region of large V_t . The amount of phenol adsorption (1) does not change for large V_t values; the value of benzene adsorption (3) is linearly dependent on V_t . Iodine adsorption is higher for low V_t values than benzene adsorption. Proceeding from analysis of the data (see Fig. 3), it can be concluded that an increase in the total pore volume in sorbents leads to a rise in the amount of adsorbed benzene and iodine not linearly and by a low value, and the sorption process may be driven by peculiarities of the surface in pores, and not by their amount. Benzene sorption under the studied conditions (static sorption of vapours) linearly increases with an increase in pore volume in carbon adsorbents. Interrelations of sorption of the substances under study

(vapours of benzene, phenol, and iodine) and the number of micropores and mesopores have not been detected in the work.

CONCLUSION

Summing up, it may be said that carbon sorbents produced by thermolysis of naturally oxidized Barzas coal impregnated with an alkaline solution mainly have the microporous structure. To produce sorbents with high sorption characteristics from the naturally oxidized Barzas coal it is required to use potassium hydroxide at the activation stage. The amount of the introduced KOH within mass ratios of (1 : 2)–(1 : 0.5) has little influence on sorption characteristics of sorbents. Therefore, for the coal under study, it is sufficient to use the coal/KOH mass ratio of 1 : 0.5. However, if for solving a task for sorption, the selection of the most efficient sorbent is required, then, the use of a large amount of alkali during activation would be appropriate. Carbon sorbents produced from naturally oxidized coal of Barzas deposit impregnated with potassium hydroxide may find applications for treatment of industrial discharges and water.

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REFERENCES

- 1 Semenova S. A., Patrakov Yu. F., *Koks i khimiya*. 2017. No. 3. P. 8–14.
- 2 Manina T. S., Fedorova N. I., Semenova S. A., Ismagilov Z. R., *Koks i Khimiya*. 2012. No. 3. P. 43–46.
- 3 Manina T. S., Fedorova N. I., Semenova S. A., Ismagilov Z. R., *Koks i Khimiya*. 2012. No. 11. P. 32–34.
- 4 Manina T. S., Fedorova N. I., Semenova S. A., Ismagilov Z. R., *Koks i Khimiya*. 2013. No. 5. P. 25–28.
- 5 Marsh H., Denis S. Y., *Carbon*. 1984. Vol. 22, No. 26. P. 603–611.
- 6 Kozlov A. P., Zykov I. Yu., Dudinkova Yu. N., Fedorova N. I., Ismagilov Z. R., *Vestn. KuzGTU*. 2017. No. 4. P. 170–175.